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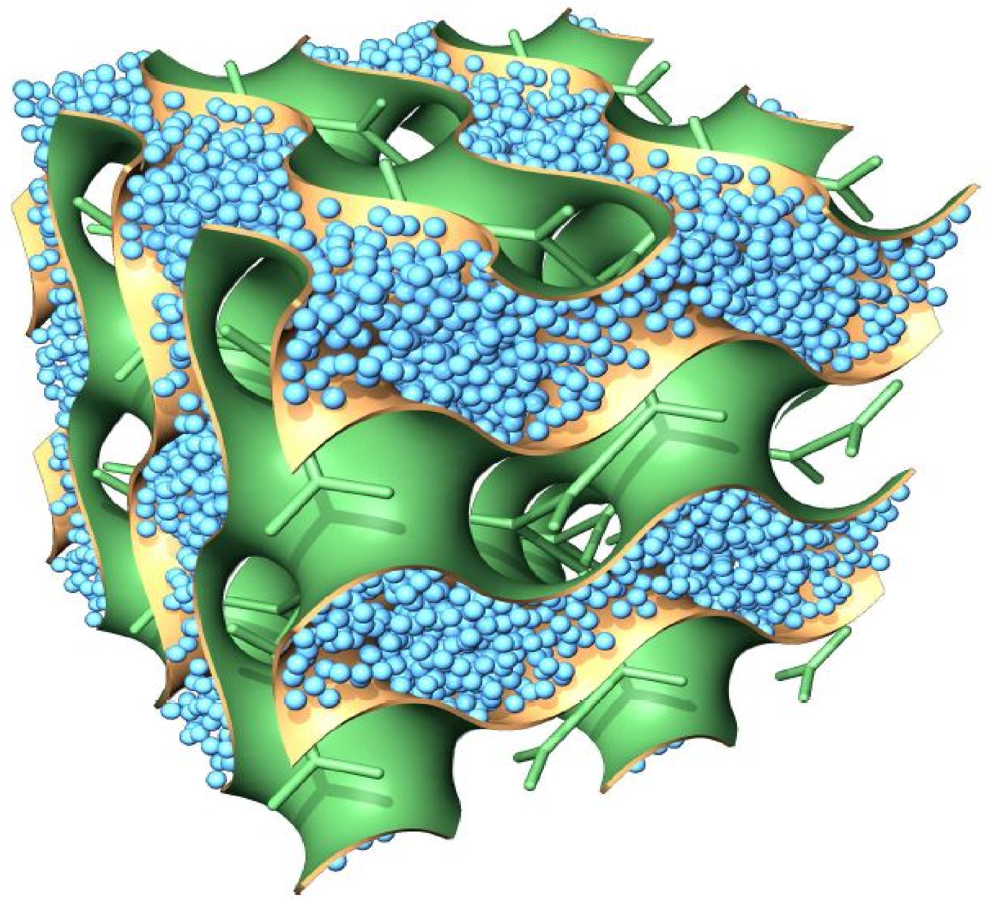
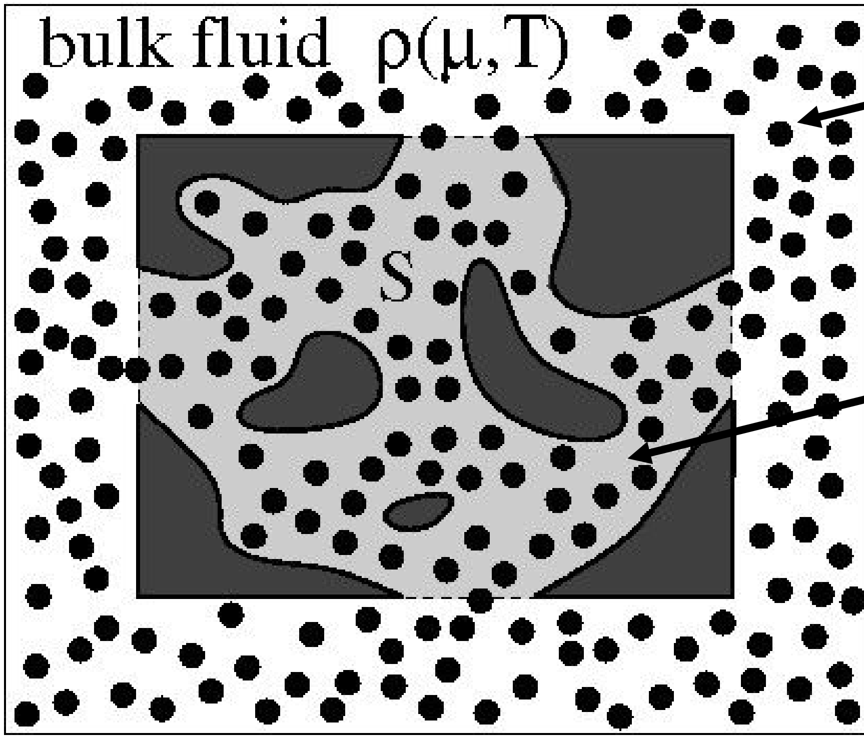


Can a confined fluid feel the topology of the confining pore?

Monte Carlo, Melbourne, Victoria 26 July 2010

Adsorption in porous medium



Reservoir

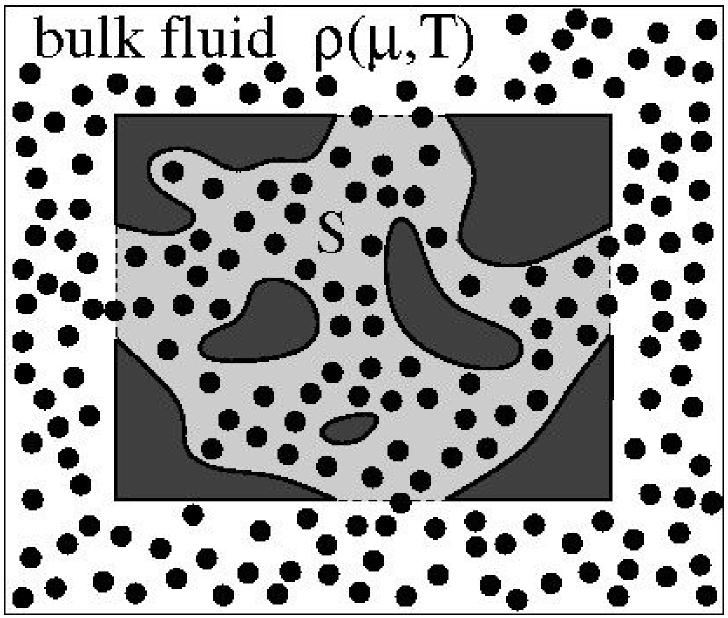
Pore S

$$\Gamma \equiv \int_S [\rho(\mathbf{r}) - \rho] dV$$

A

Which morphological characteristics of S determine the adsorption Γ?

Which morphological characteristics of S determine the adsorption Γ?



$$\Gamma \equiv \int_S [\rho(\mathbf{r}) - \rho] dV$$

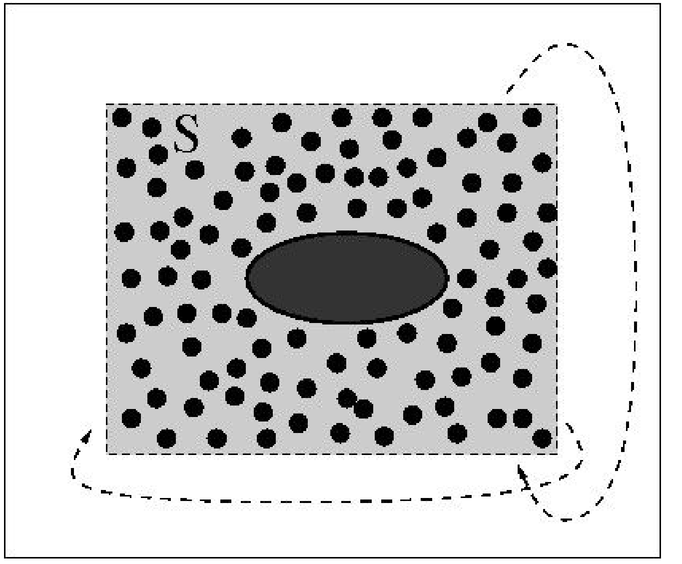
A

Volume of pore

Surface Area of Interface

$$\Gamma(S,\mu,T) = p(\mu,T)\, V[S] + s(\mu,T)\, A[S] + ???$$

König, Mecke, Roth, PRL 93(16), 160601 (2004):



For hard spheres with ξ << pores, the grand-canonical potential Ω is :

(1) Motion-invariant

(2) Continuous w.r.p. to small changes in S

(3) approximately additive $\Omega[S_1 \cup S_2] = \Omega[S_1] + \Omega[S_2] - \Omega[S_1 \cap S_2]$

Hadwiger Theorem from Integral geometry:

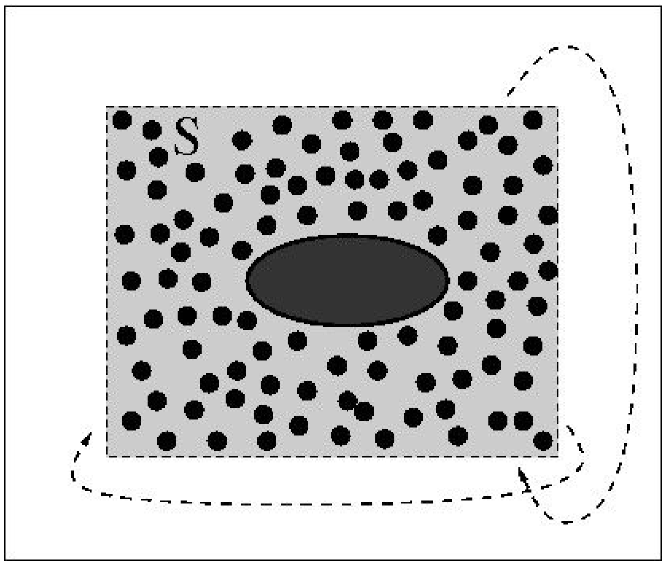
Any motion-invariant, continuous and additive Ω[S] is a linear combination of the Minkowski functionals V[S], A[S], C[S], X[S].

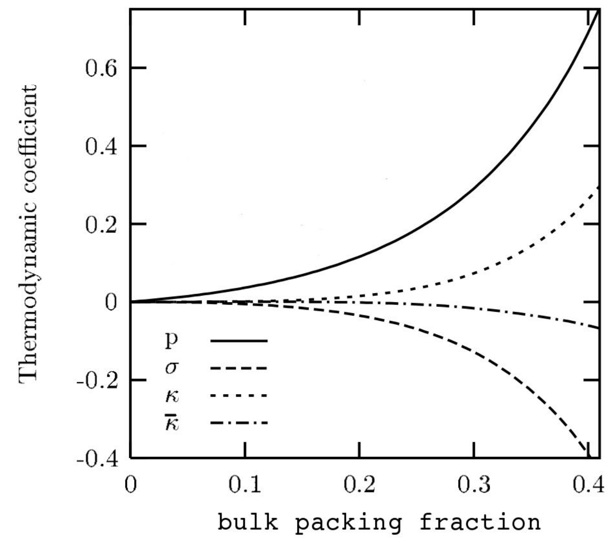
$$C = \int_{\partial S} H dA \qquad X = \int_{\partial S} K dA$$

$$\Omega[S] = -pV[S] + \sigma A[S] + \kappa C[S] + \bar{\kappa} X[S]$$

König, Mecke, Roth, PRL 93(16), 160601 (2004):

DFT (Rosenfeld) for Pores that are complement of convex shapes





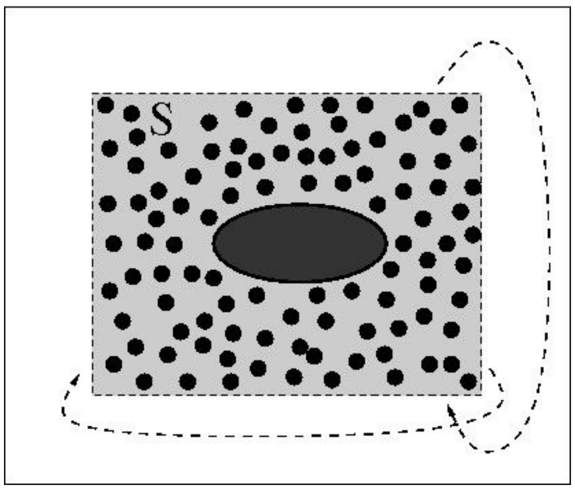
$$\Omega[S] = -pV[S] + \sigma A[S] + \kappa C[S] + \bar{\kappa} X[S]$$

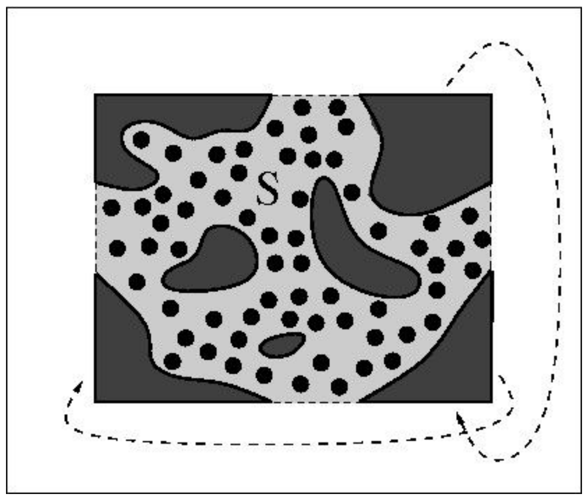
Does

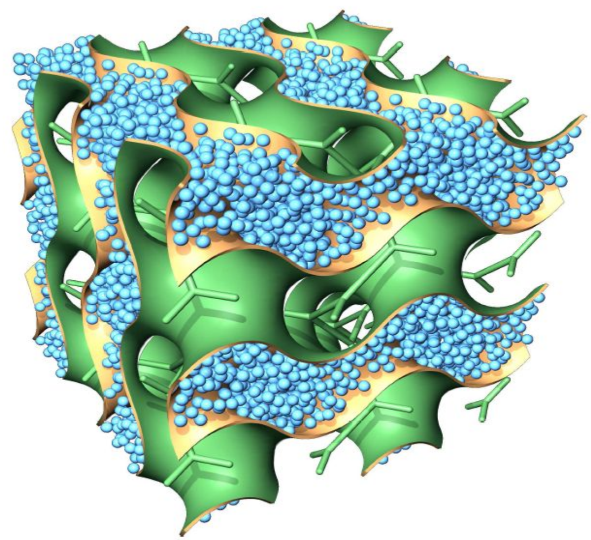
$$\Omega[S] = -pV[S] + \sigma A[S] + \kappa C[S] + \bar{\kappa} X[S]$$

also hold for

Non-convex pore geometries!?

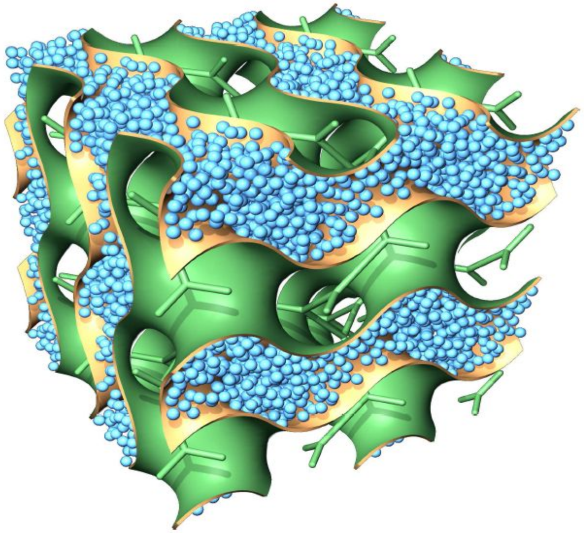




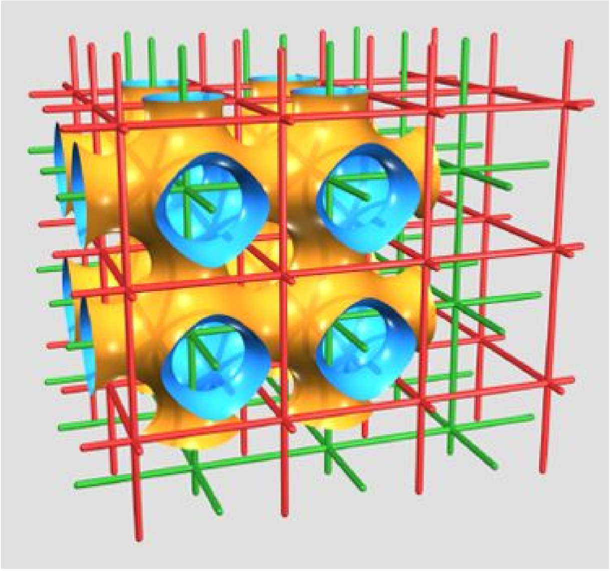


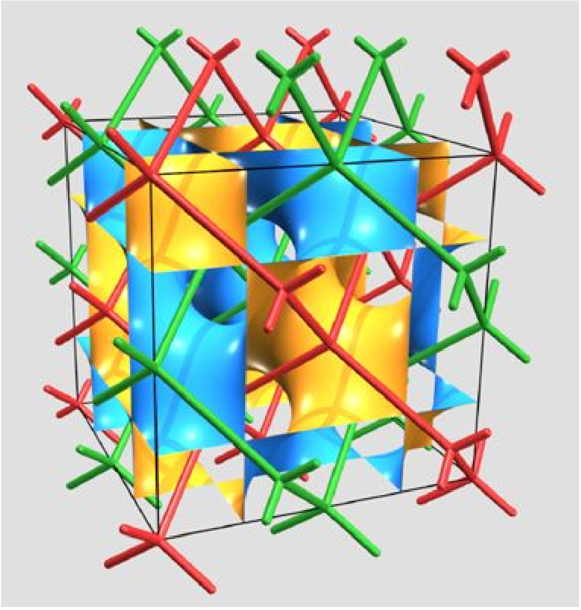
Triply-periodic Minimal surfaces

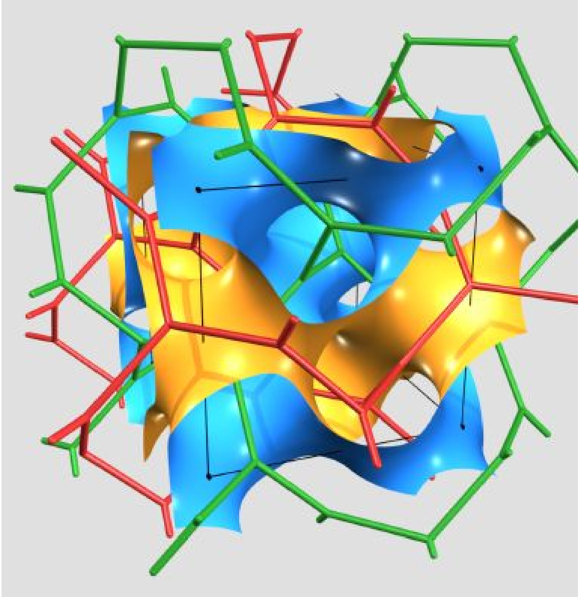
Triply-Periodic Minimal Surfaces



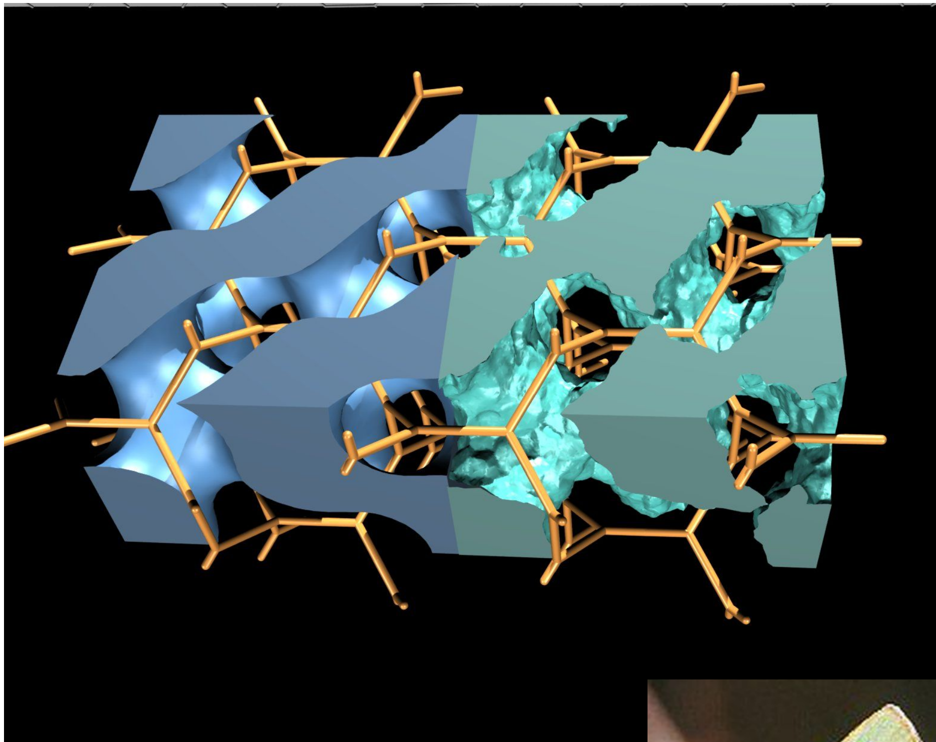
- mean curvature H = 0 → C[S] = 0
- Periodic
- Divide space into a solid & a void network domain
- Porosity 50%
- Large catalogue of TPMS available: P, D, G, H, IWP,...
- Exact Weierstrass parameterization → accurate triangulations

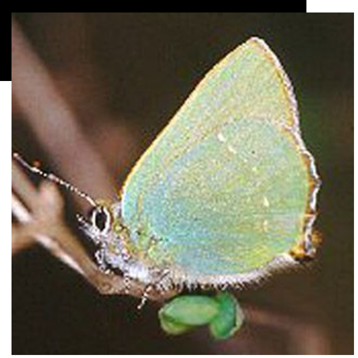




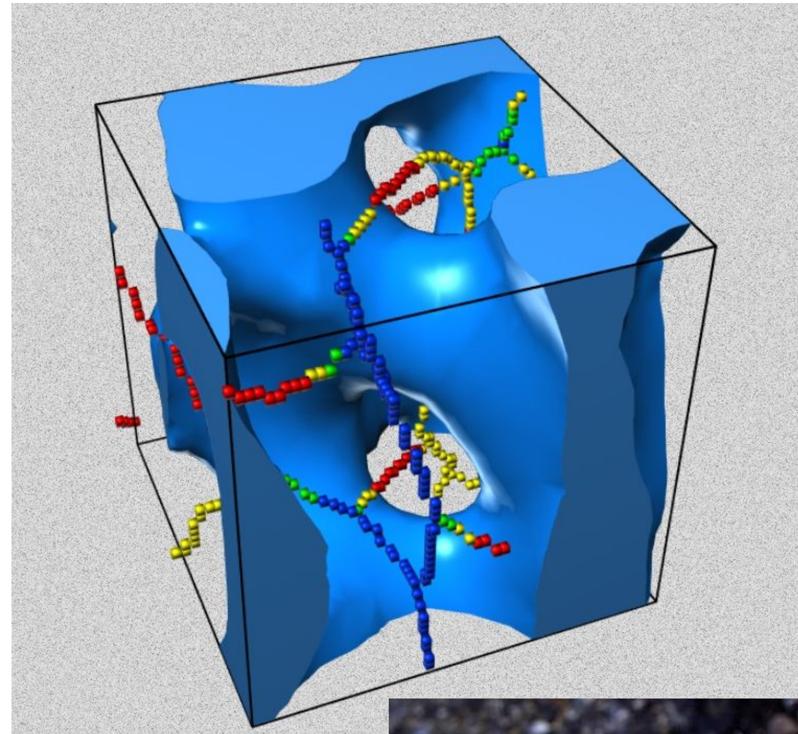


Box = $(\sim 500\ \mathrm{nm})^3$





Box = $(\sim 20\ \mu\mathrm{m})^3$



Chitin Photonic crystals in butterfly wing

Optimal compromise between mechanical and transport properties in Biominerals

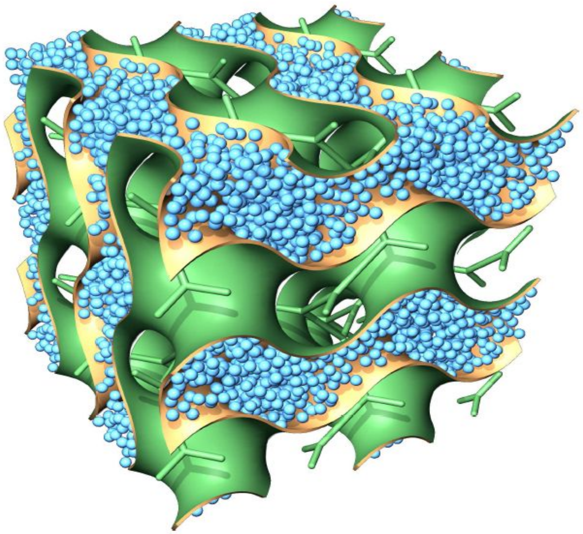
Grand-canonical Monte Carlo of Spheres confined by triangulated domains

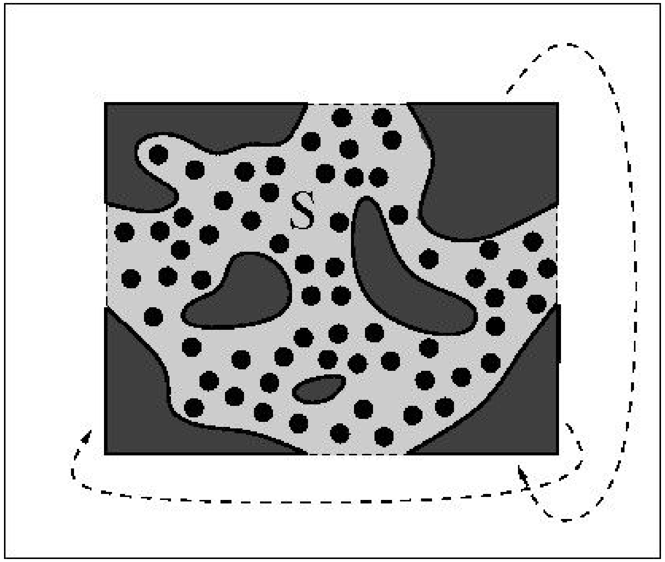
Distance to surface

$$U_{sub}(\mathbf{r}) = \begin{cases} 0 & \text{if } d(\mathbf{r}) > D/2 \\ \infty & \text{otherwise} \end{cases} .$$

$$U_{sph}(\mathbf{r}, \mathbf{r}') = \begin{cases} 0 & \text{if } |\mathbf{r} - \mathbf{r}'| > D \\ \infty & \text{otherwise} \end{cases} .$$

$$U(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{i=1}^{N} U_{sub}(\vec{r}_i) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} U_{sph}(\vec{r}_i, \vec{r}_j)$$

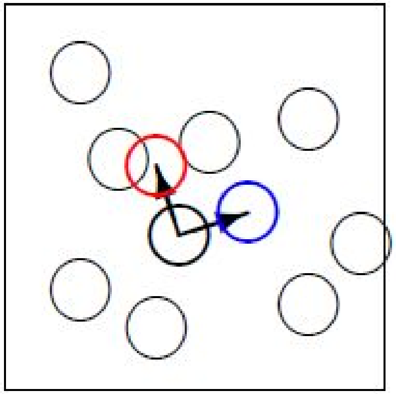




- Periodic BC
- Simul. box = transl. unitcell of surface
- Surface as triangulation

Grand-canonical Monte-Carlo II

2. Monte-Carlo move: perform one of the three actions with equal probability
   - move a randomly chosen particle
   - insert a particle at a random position
   - delete a randomly chosen particle



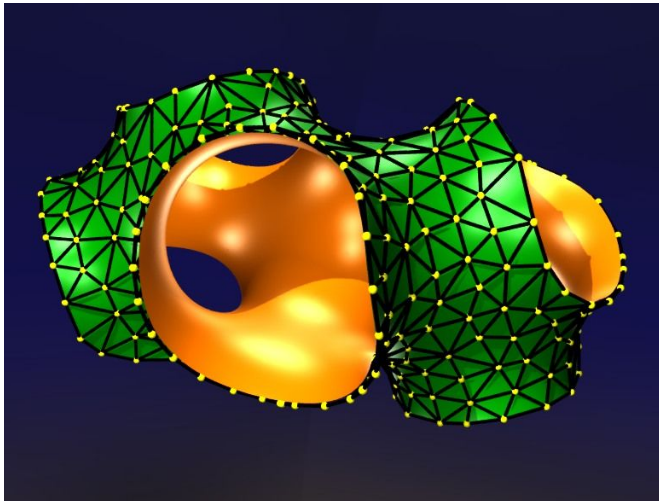
Accepting probabilities:

- every action is rejected if it creates overlap
- if not:
  - moves always accepted
  - insertion and deletion with certain probability:

$$\mathrm{acc}(N \to N+1) = \min\left(1,\ \frac{V}{N+1} \cdot \frac{\exp(\beta\mu)}{\Lambda^3}\right)$$

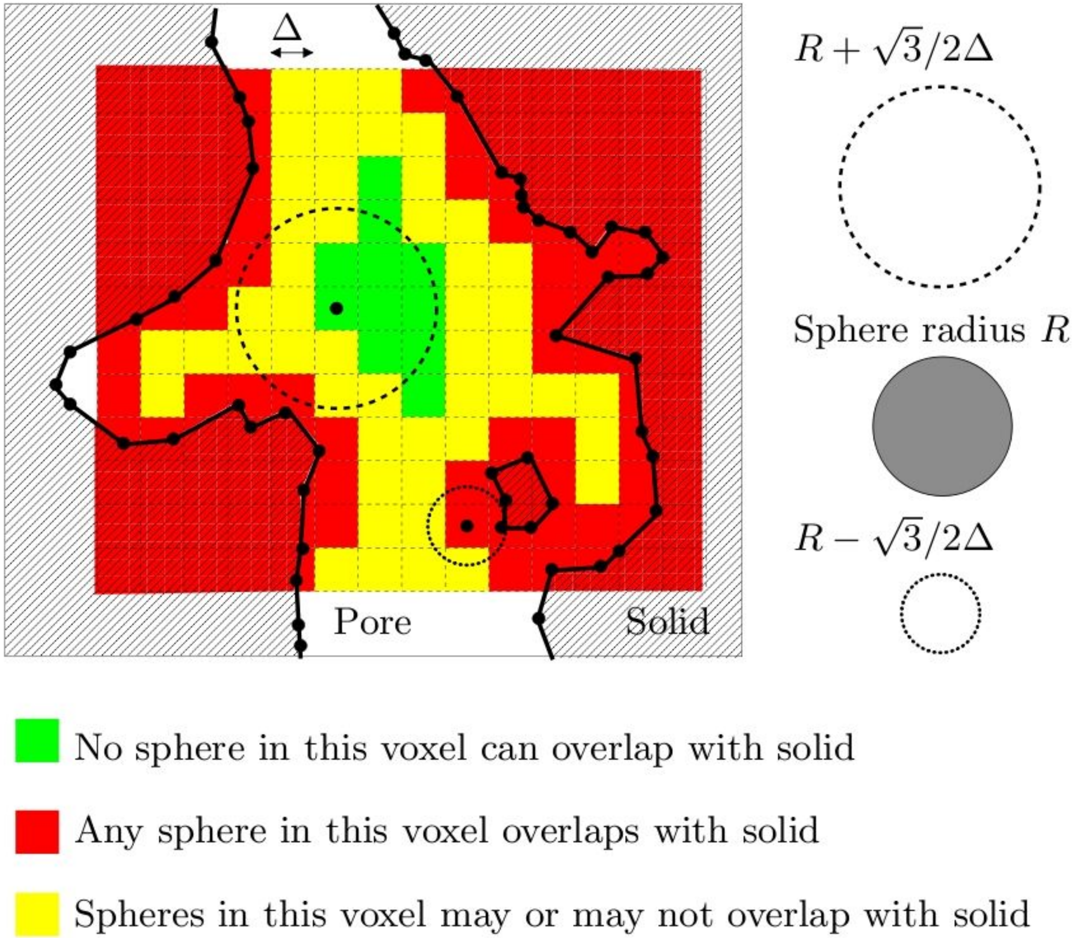
$$\mathrm{acc}(N \to N-1) = \min\left(1,\ \frac{N}{V} \cdot \frac{\Lambda^3}{\exp(\beta\mu)}\right)$$

Fast but precise Substrate-Overlap Predicate



$$U_{sub}(\mathbf{r}) = \begin{cases} 0 & \text{if}\, d(\mathbf{r}) > D/2 \\ \infty & \text{otherwise} \end{cases} .$$

- Fast (slows down simulation by factor 2-5)
- Treat geometry as exactly as possible

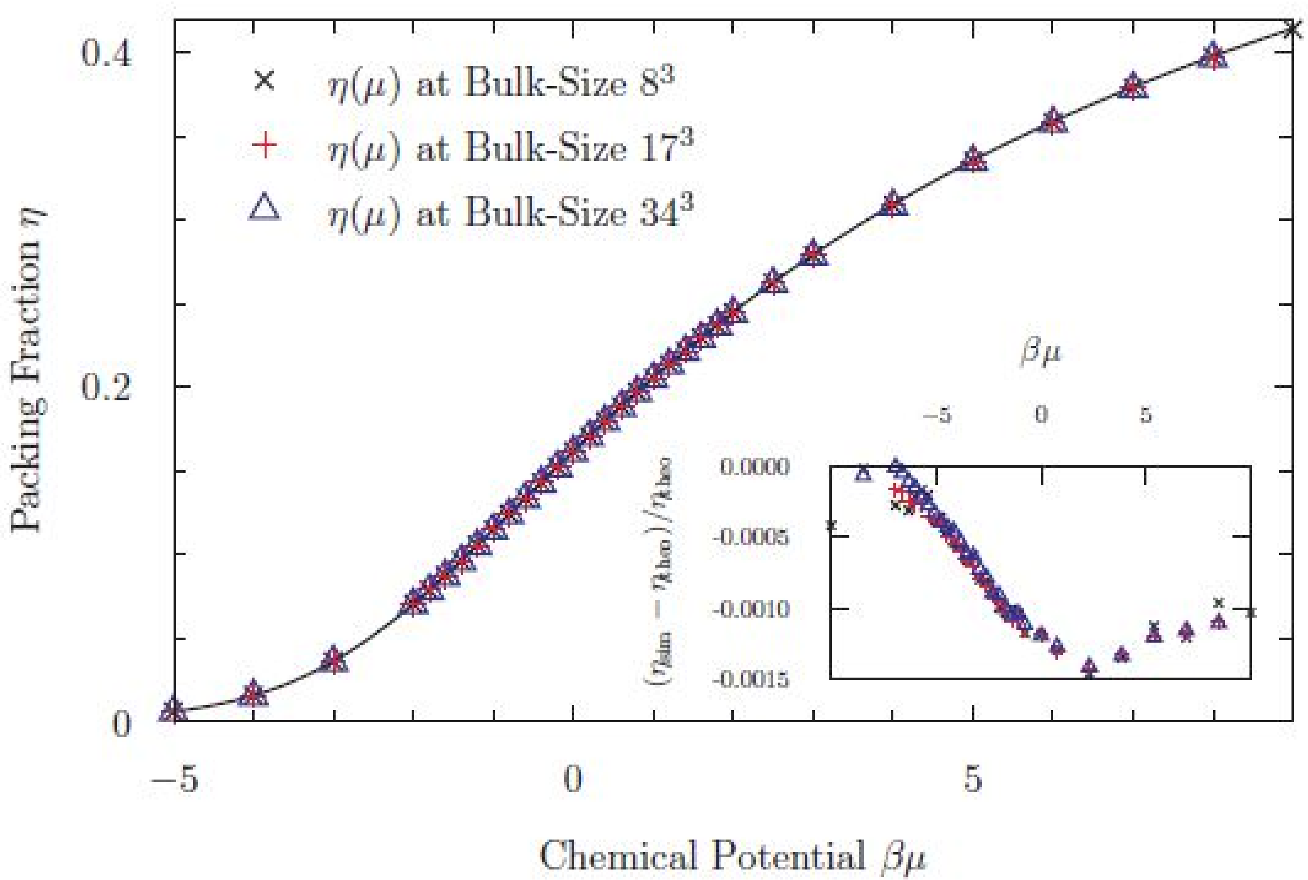


Precise overlap test with triangles

Bulk (no substrate): density vs chemical potential

Comparison with Carnahan-Starling theory:

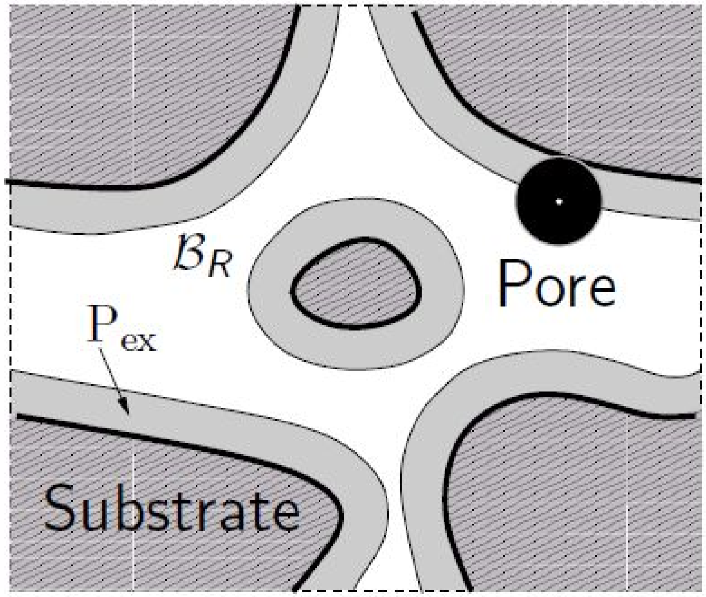
Result:



Density of Confined Fluid

V_{Sph} volume of spheres and $V(\mathcal{B}_R)$ volume of accessible pore space:

$$\eta_0 = \langle N \rangle \cdot \frac{V_{\mathrm{Sph}}}{V(\mathcal{B}_R)} = -\frac{\partial \Omega(T,\mu)}{\partial \mu} \cdot \frac{V_{\mathrm{Sph}}}{V(\mathcal{B}_R)}$$



- Trivial excluded volume effect removed
- Propagation of order from substrate into liquid => morphology effect

Morphometric Approach (Klaus Mecke, Roland Roth)

$$\Omega[S] = -p \cdot V[S] + \sigma \cdot A[S] + \kappa \cdot C[S] + \overline{\kappa} \cdot X[S]$$

White Bear DFT [2] $\Rightarrow$ Coefficients $p, \sigma, \kappa, \overline{\kappa}$ as function of bulk density η (Sphere radius R)

$$\beta p = \frac{3\eta}{4\pi R^3} \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \quad , \quad \beta\sigma = \frac{\eta(2+(3-2\eta)\eta) - (1-\eta)^2 \ln(1-\eta)}{4(1-\eta)^2 \pi R^2}$$

$$\beta\kappa = \frac{(5-\eta)\eta}{(1-\eta)R} + 2\ln(1-\eta) \quad , \quad \beta\overline{\kappa} = -\ln(1-\eta)$$

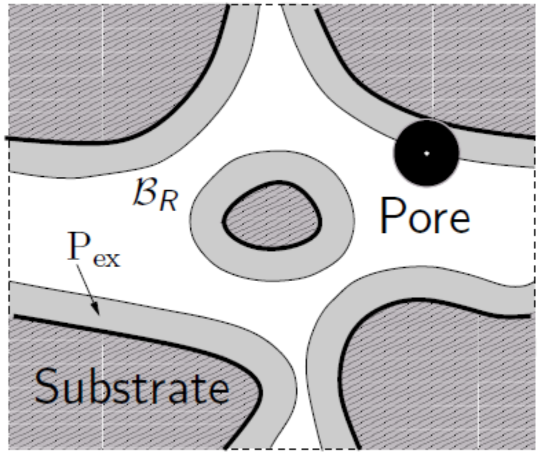
Explicit formula for confined fluid density

$$\eta_0 = -\frac{\partial\Omega(T,\mu)}{\partial\mu} \cdot \frac{V_{\mathrm{Sph}}}{V(\mathcal{B}_R)}$$

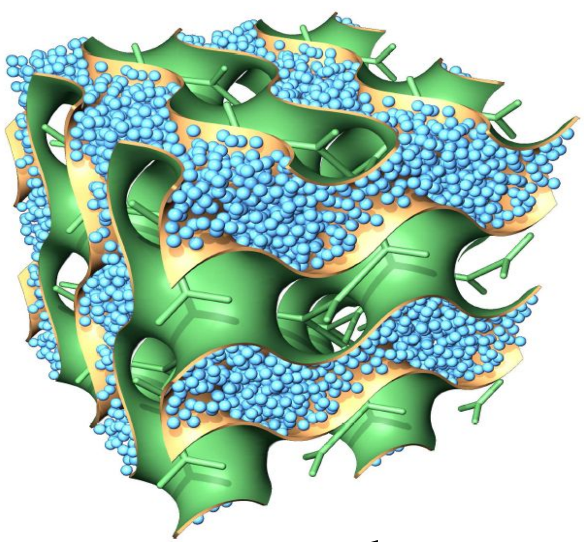
$$= \frac{V_{\mathrm{Sph}}}{V(\mathcal{B}_R)} \Big(\rho_{\mathrm{bulk}} \cdot \mathbf{V} + \frac{(\eta-1)\eta(3+\eta(6+\eta(2\eta-5)))}{4(1+\eta(4+(\eta-2)^2\eta))\pi R^2} \cdot \mathbf{A}$$

$$- \frac{(\eta-1)^2\eta(3+\eta^2)}{1+\eta(4+(\eta-2)^2\eta)R} \cdot \mathbf{C} - \frac{(\eta-1)^3\eta}{1+\eta(4+(\eta-2)^2\eta)} \cdot \mathbf{X} \Big)$$

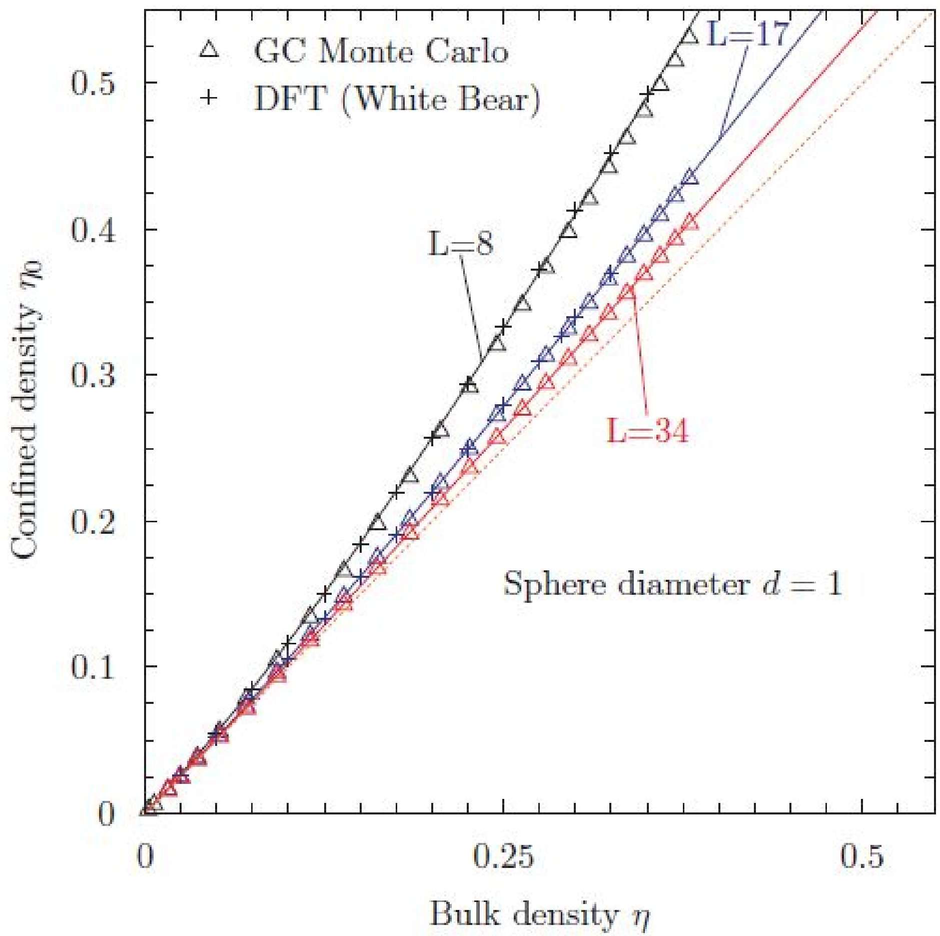
Fluids in Gyroid



$$\eta_0 = \langle N \rangle \cdot \frac{V_{\text{Sph}}}{V(\mathcal{B}_R)}$$



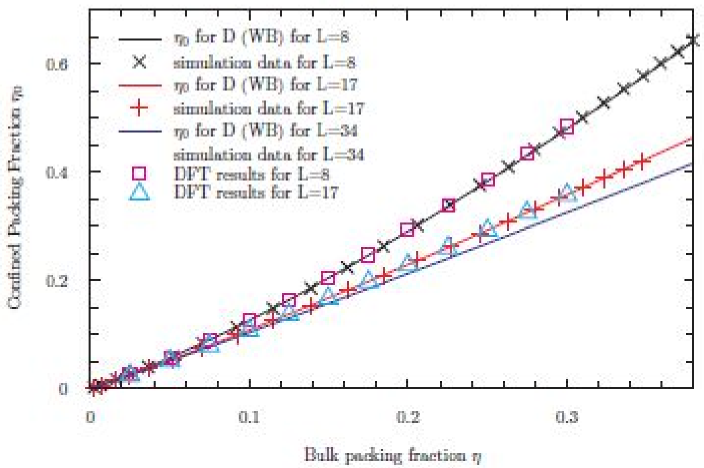
2L



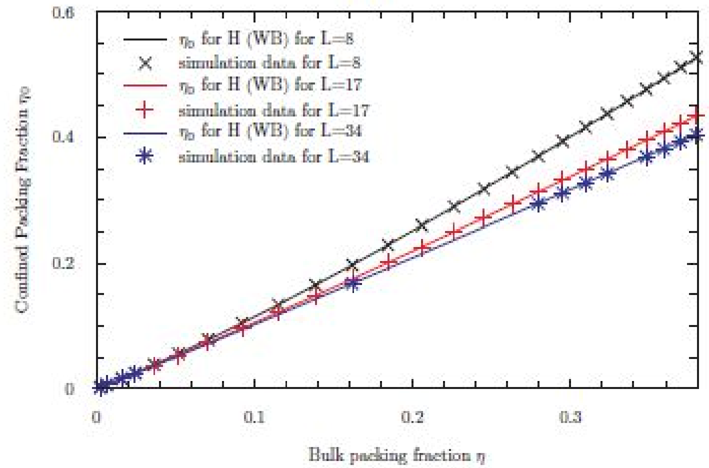
- Volume & surface term dominant
- But, topology also matters

η_0 for other Surfaces

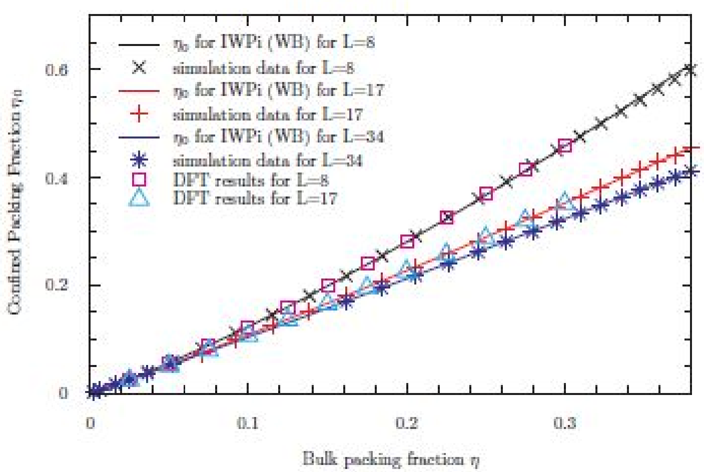
D



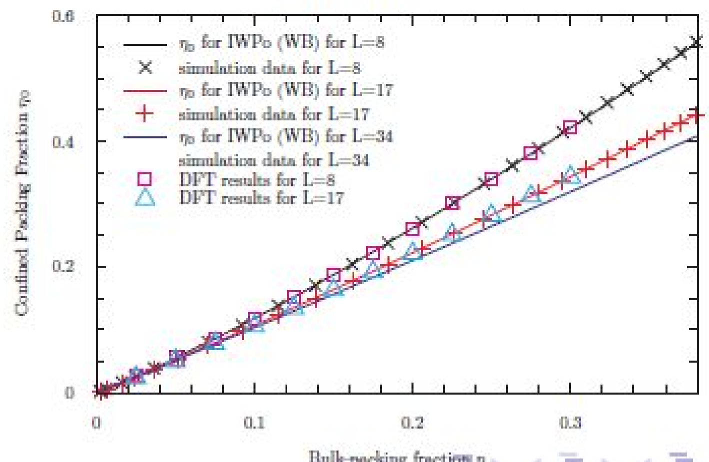
H



IWPi

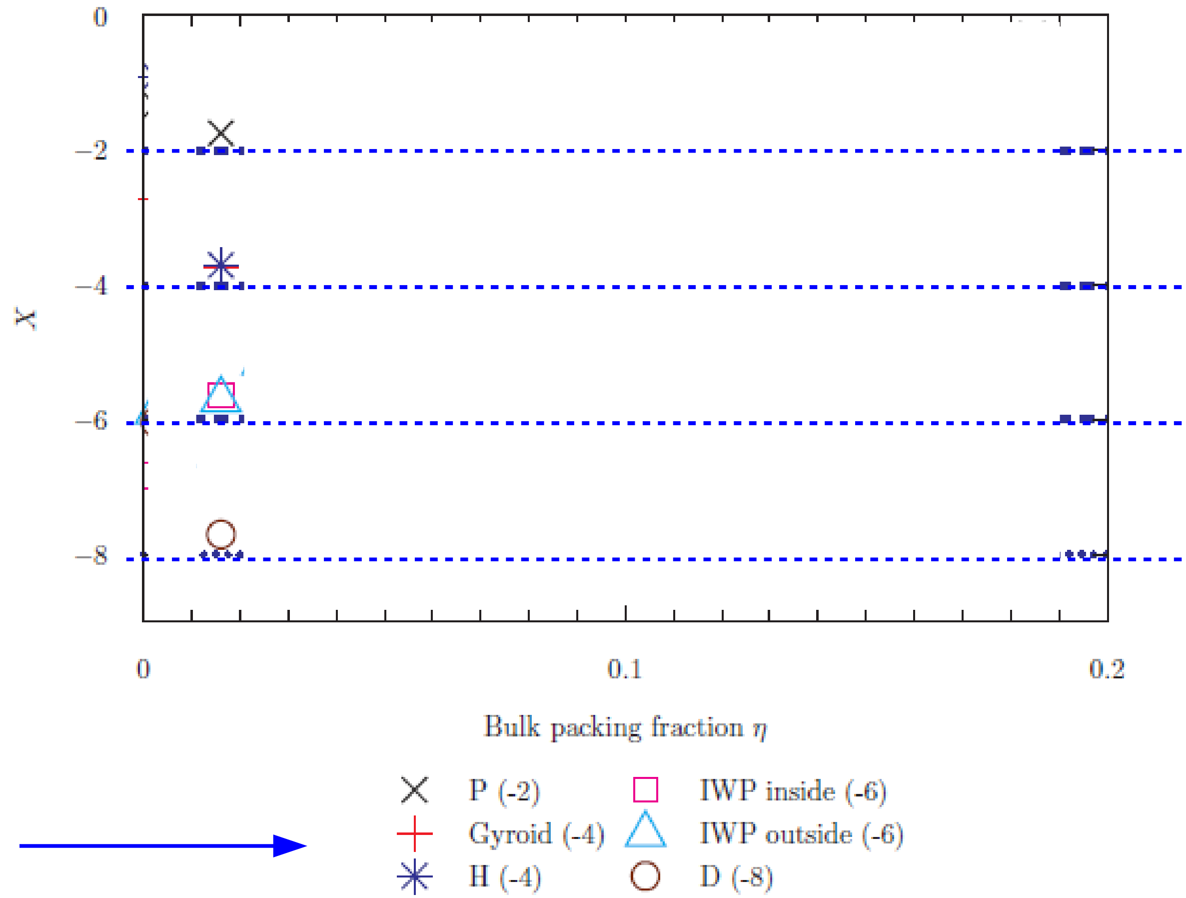


IWPo



Can a fluid feel the topology of a pore?

$$\eta_0 = \eta_0(V, A, C, X) \qquad \Rightarrow \qquad X = X(\eta_0, V, A, C)$$

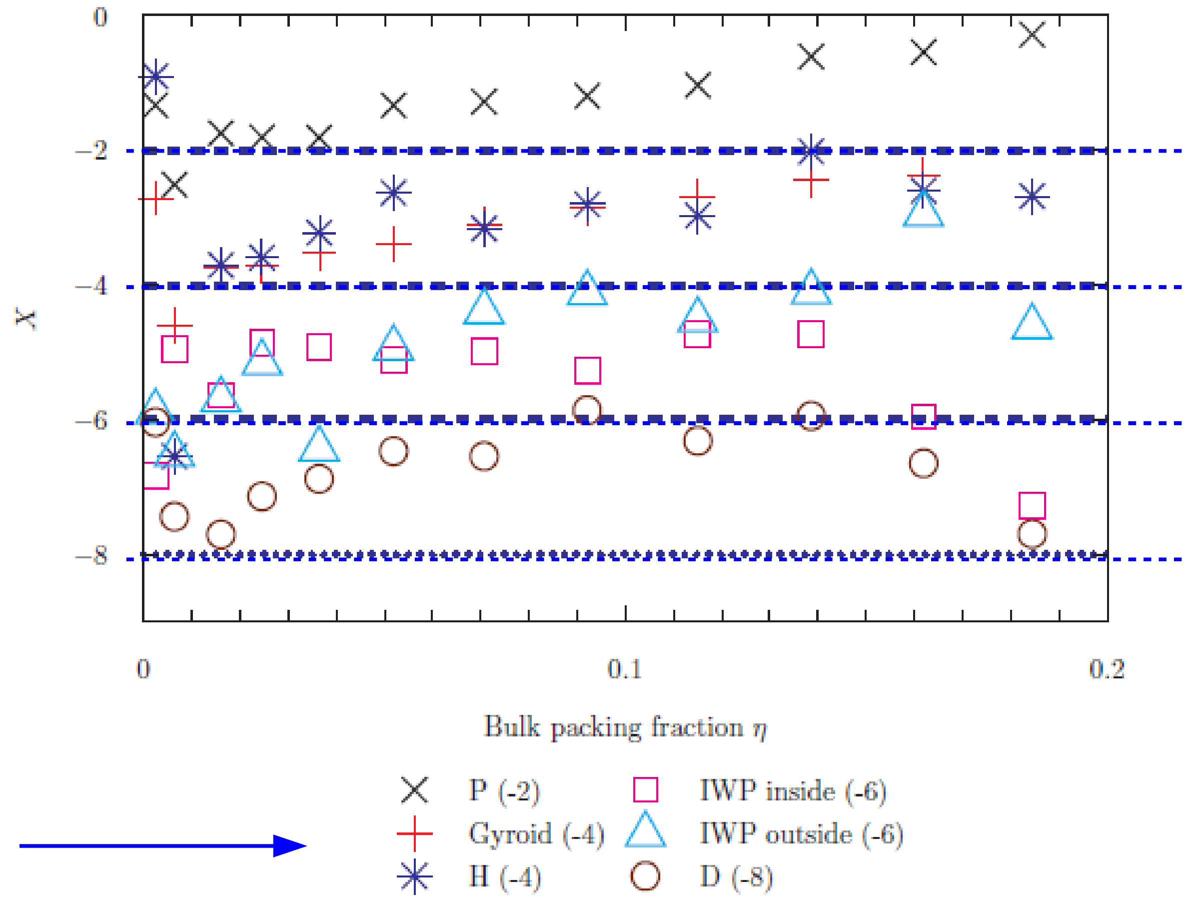


Seems like it can!

Different geometries
with different X

Can a fluid feel the topology of a pore?

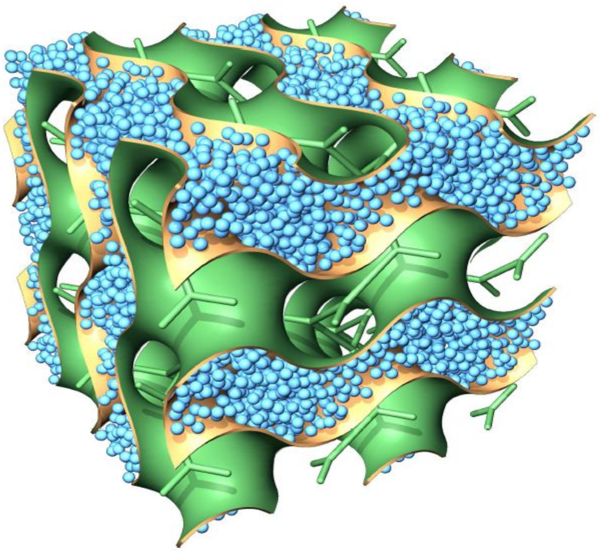
$$\eta_0 = \eta_0(V, A, C, X) \qquad \Rightarrow \qquad X = X(\eta_0, V, A, C)$$



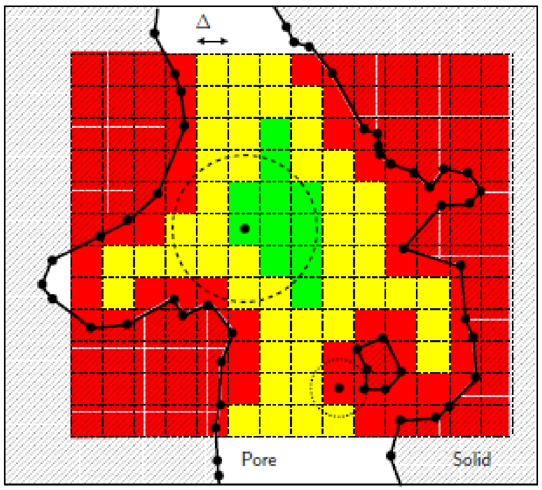
Resolution problems?

Different geometries
with different X

Morphometric approach to confined equilibrium fluids



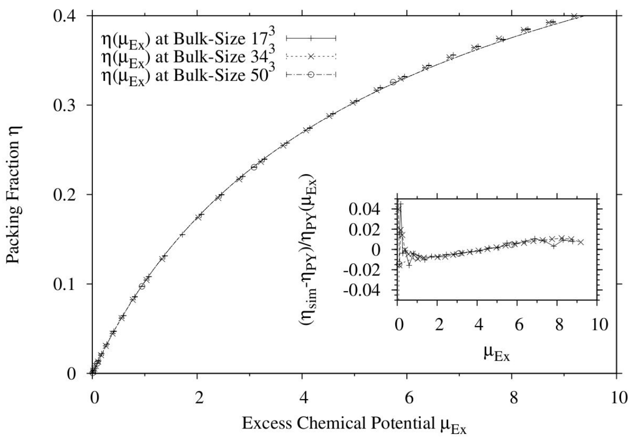
- Adsorption in confining pores
- Morphological determinants: V, A, C, X
- Fast Lookup-Table for triangulated pores
- Topology matters (at least a little bit)



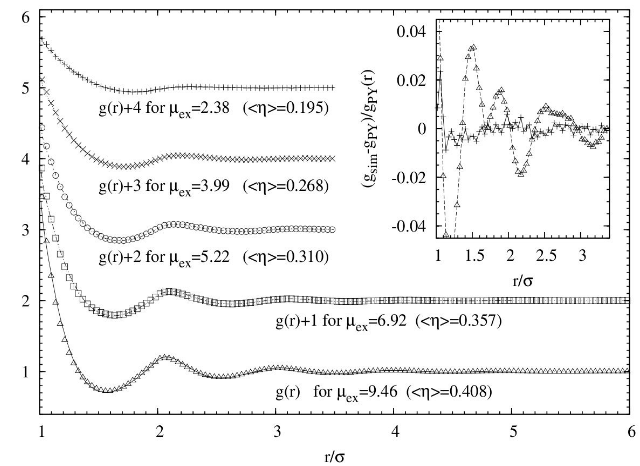
www.theorie1.physik.uni-erlangen.de/gerd

Some simple tests

Bulk test: density vs chemical potential



Bulktwo-point correlations



Density profile between two parallel plates
[Henderson et al., J. Stat.Phys., 89, 233 (1997)]